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Research Paper

Hydrogeochemical and multi-tracer investigations of arsenic-affected aquifers in semi-arid West Africa

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ABSTRACT

The semi-arid Sahel regions of West Africa rely heavily on groundwater from shallow to moderately deep (<100 m b.g.l.) crystalline bedrock aquifers for drinking water production. Groundwater quality may be affected by high geogenic arsenic (As) concentrations (>10 µg/L) stemming from the oxidation of sulphide minerals (pyrite, arsenopyrite) in mineralised zones. These aquifers are still little investigated, especially concerning groundwater residence times and the influence of the annual monsoon season on groundwater chemistry. To gain insights on the temporal aspects of As contamination, we have used isotope tracers (noble gases, ³H, stable water isotopes (²H, ¹⁸O)) and performed hydrochemical analyses on groundwater abstracted from tube wells and dug wells in a small study area in southwestern Burkina Faso. Results revealed a great variability in groundwater properties (e.g. redox conditions, As concentrations, water level, residence time) over spatial scales of only a few hundred metres, characteristic of the highly heterogeneous fractured underground. Elevated As levels are found in oxic groundwater of circum-neutral pH and show little relation with any of the measured parameters. Arsenic concentrations are relatively stable over the course of the year, with little effect seen by the monsoon. Groundwater residence time does not seem to have an influence on As concentrations, as elevated As can be found both in groundwater with short (<50 a) and long (>10³ a) residence times as indicated by ³He/⁴He ratios spanning three orders of magnitude. These results support the hypothesis that the proximity to mineralised zones is the most crucial factor controlling As concentrations in the observed redox/pH conditions. The existence of very old water portions with residence times >10³ years already at depths of <50 m b.g.l. is a new finding for the shallow fractured bedrock aquifers of Burkina Faso, suggesting that overexploitation of these relatively low-yielding aquifers may be an issue in the future.

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1. Introduction

Shallow to moderately deep (<100 m b.g.l.) groundwater from fractured, crystalline bedrock aquifers constitutes the most important drinking water resource in rural and peri-urban areas of many

sub-Saharan countries (MacDonald and Calow, 2009; MacDonald et al., 2012), for example in Burkina Faso, West Africa (Barbier et al., 2006). However, in this region, groundwater quality can be affected by high levels of geogenic arsenic (As), released through the oxidation of sulphide minerals occurring in the volcano-sedimentary schists and volcanic rocks of the Birimian formation (Ahoulé et al., 2015). Such As contamination has been shown to contaminate groundwater throughout Burkina Faso (Smedley et al., 2007; Barro-Traoré et al., 2008; Somé et al., 2012; Sako et al., 2016; Bretzler et al., 2017) and neighbouring Ghana (Smedley, 1996; Asante et al., 2007; Buamah et al., 2008). An estimated 560,000 people are potentially

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exposed to elevated As concentrations via their drinking water in Burkina Faso alone (Bretzler et al., 2017). The serious and chronic health effects of prolonged exposure to As-contaminated water include the development of a variety of cancers as well as developmental, neurological and cardiovascular diseases (Argos et al., 2010; Naujokas et al., 2013).

In comparison to the well-known cases of large-scale groundwater As contamination in South and South-East Asia which have been extensively addressed, geogenic As in the fractured crystalline bedrock aquifers of West Africa is less thoroughly investigated (Nikiema et al., 2013; Ahoulé et al., 2015). To the best of our knowledge, no work has yet looked into the influence of the annual monsoon on As concentrations, nor has the residence time of As contaminated groundwater in this region been investigated. Tracers such as noble gases, stable water isotopes (^2H , ^{18}O) and tritium (^3H) have shed light on groundwater mobility and flow paths of high-As waters in South-East Asia (Klump et al., 2006; McArthur et al., 2010). Isotope tracers as tools for determining groundwater origin and residence times have rarely been employed in the West African Sahel. The few existing studies have mostly focussed on aquifers of the large sedimentary basins, for example the Chad basin (Chad, Nigeria), the Iullemeden basin (Niger) and the Taoudeni basin (western Burkina Faso, Mali) (Beyerle et al., 2003; Rueedi et al., 2005a, b; Maduabuchi et al., 2006; Huneau et al., 2011). Age-dating of deep groundwater (>100 m b.g.l.) of these sedimentary formations using ^{14}C and noble gases revealed residence times of several thousands to tens of thousands of years, with recharge having occurred during wetter and cooler climatic periods in the Sahel. On the other hand, the shallow aquifers (both sedimentary formations and weathered crystalline bedrock) used extensively for drinking water production in West Africa are thought to contain mostly modern groundwater with residence times of less than 65 years (Lapworth et al., 2013) with some authors estimating that groundwater abstraction can be developed substantially without over-exploitation (Martin and Van De Giesen, 2005; MacDonald et al., 2012). The application of tracers also capable of identifying old water components (e.g. ^4He) in the shallow crystalline bedrock aquifers has yet to be carried out.

Considering large population growth (Gerland et al., 2014) and planned intensification of irrigated agriculture in sub-Saharan Africa (MacDonald et al., 2012), groundwater use will increase in the future and both water quality assessments and the sustainability of increased exploitation are vital information for decision makers. Regarding these challenges and to gain insights on the temporal aspects of As groundwater contamination, we used tracers (noble gases, ^3H , ^2H , ^{18}O) and performed hydrochemical analyses and seasonal sampling on a shallow to moderately deep groundwater system affected by geogenic As contamination. Recently, a broad, nationwide groundwater quality survey revealed the widespread occurrence of arsenic-affected aquifers in Burkina Faso (Bretzler et al., 2017). Following up on these findings, the present study focuses on small-scale heterogeneities in these aquifers, investigated in a small study area ($\sim 80\text{ km}^2$). The properties of fractured rock aquifers are generally difficult to predict and in Burkina Faso, detailed, site-specific information on geological and hydrogeological conditions at depth, as well as borehole characteristics are usually not available. The chosen approach can give indications on groundwater residence times and environmental conditions at the time of recharge and may also aid in understanding the occurrence, distribution and geochemistry of arsenic-affected groundwater.

2. Study area

The study site of Poura is located about 250 km southwest of Burkina Faso's capital city Ouagadougou and is typical of the

relatively flat, highly weathered Central Plateau of Burkina Faso (Fig. 1). The studied area covers about 80 km^2 and terrain elevations range from 330 m a.s.l. in the slightly hilly east to 230 m next to the Mouhoun river in the west. The administrative community of Poura has about 10,000 inhabitants and comprises the main town of Poura Mine, as well as several nearby villages (Poura Village, Kankele, Darsalam, Toécin, Basnééré, Mouhoun 3, Bologo) (Fig. 1). Poura lies within the Sahelian-Soudanian climate zone, experiencing dry conditions for most of the year, with a distinct wet season from June to September. For the years 2003–2015, the mean annual precipitation in the town of Boromo (25 km northwest of Poura) was 930 mm, mean annual potential evapotranspiration 1800 mm and the mean annual minimum/maximum temperatures $22.3\text{ }^\circ\text{C}$ and $35.5\text{ }^\circ\text{C}$ (Source: Direction de la Météorologie du Burkina). Poura was the location of Burkina Faso's first state owned gold mine, in operation from 1961 to 1966 and from 1984 to 1996. Currently, informal artisanal goldmining is widespread at several locations within the study area.

2.1. Geology

Apart from sedimentary rocks belonging to the Taoudeni Basin and the Continental Terminal formation, the geology of Burkina Faso is dominated by crystalline bedrock of varying lithologies formed during the Paleoproterozoic era (2300–1600 Ma) (Fig. 1). Large granitic bodies (granite, granodiorite, tonalite) of the Eburnean orogeny occur next to belts of meta-sedimentary and (meta)-volcanic rocks that cross the country from SW–NE and belong to the Birimian formation (Castaing et al., 2003) (Fig. 1). The study site of Poura is located on one such Birimian belt (the Boromo greenstone belt) in a shear zone dominated by N–S trending structures. Poura is underlain by series of intermediate to basic volcanic rocks (andesite, andesitic tuff, rhyolite) and some sandy conglomerates belonging to the Tarkwaïen group that act as host rocks for mesothermal gold-quartz vein deposits (see detailed geological map in section 4.1) (Milési et al., 1992; Kote et al., 2003). Occurring with these quartz veins are sulphide minerals, predominantly pyrite (FeS_2) and arsenopyrite (FeAsS). In addition to these quartz vein-associated gold deposits, disseminated-style deposits are found within a few kilometres of Poura Mine at the gold mining districts of Larafella and Loraboué, where gold and sulphide minerals occur disseminated within the host rock (Bamba et al., 2002; Béziat et al., 2008).

2.2. Hydrogeology

The fractured rock aquifers of Burkina Faso (and large parts of West Africa) are a result of intense alteration weathering processes leading to a characteristic weathering profile. Numerous studies in the last 20 years have shown that weathering processes, rather than tectonics, are primarily responsible for the creation of the dense fissure and fracture network that forms these aquifers (Courtois et al., 2010; Lachassagne et al., 2011; Koita et al., 2013; Soro et al., 2017). A typical weathering profile is made up of, from top to bottom, (i) a few metres of ferricrete/laterite or iron/bauxite crust, (ii) several tens of metres of clayey saprolite resulting from prolonged, in-situ decomposition of the parent rock through weathering, (iii) several tens of metres of densely fissured parent rock and (iv) the fresh, unfractured bedrock. The saprolite layer can in itself be divided into a so-called alloterite sub-unit consisting mostly of clays, lying above a less weathered isalterite sub-unit (lower clay content, parent rock structure preserved). The thicknesses of the individual layers can vary greatly according to lithology and ancient or current topography and erosion processes (Bamba, 1996; Koita et al., 2013).

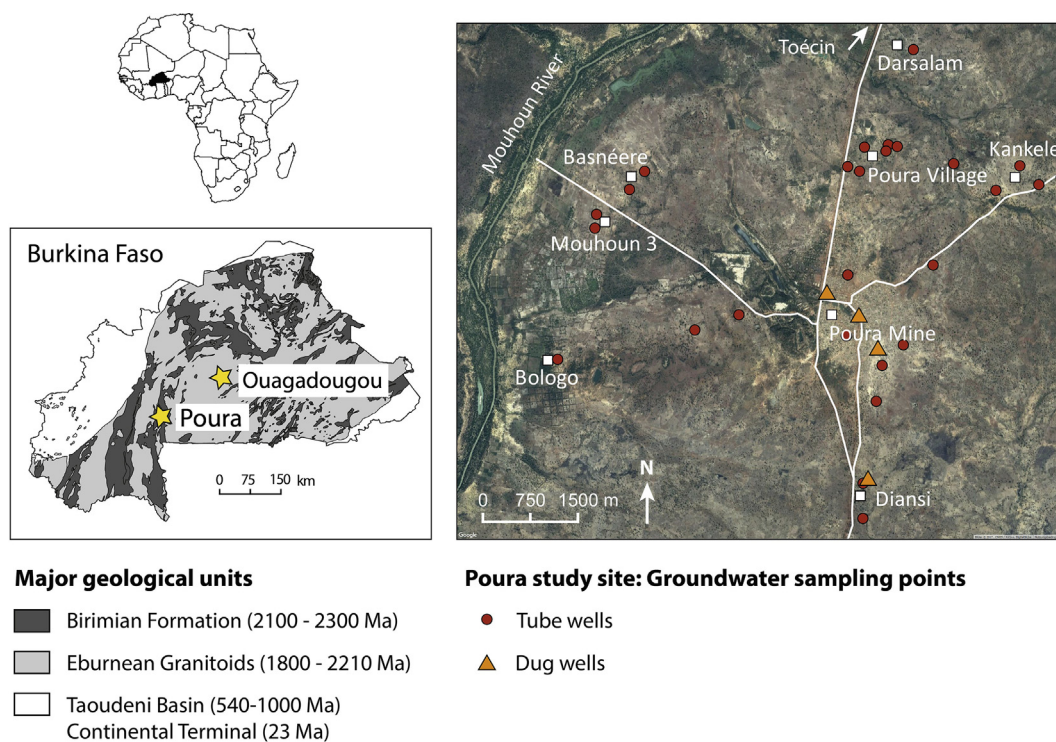


Figure 1. Location of the study area and groundwater sampling points.

The saprolite layer has greater groundwater storage (Compaore et al., 1997), whereas the fissured/fractured bedrock is seen to have a more conductive function due to its increased secondary permeability. From the few available borehole logs and literature sources available for Poura and its vicinity (e.g. Bamba, 1996), it could be deduced that saprolite and fissured layer thicknesses vary greatly within this small area, with average thicknesses of 27 m and 33 m respectively (Stolze, 2015).

Groundwater in the study area is exploited for domestic purposes via tube wells equipped with hand pumps. Shallow dug wells (5–25 m deep) usually tap groundwater from the saprolite layer and are vulnerable to seasonal water level changes and surface pollution. Tube wells with depths at 36–90 m (mean depth 61 m, $n = 20$) are often drilled all the way to the fresh bedrock. This is a typical tube well depth distribution in Burkina Faso, as shown by Courtois et al. (2010) who investigated the properties of nearly 15,000 tube wells. Borehole screens are placed within the fissured layer, often in multiple layers (up to three screened sections per borehole) corresponding to fissures with high hydraulic conductivity (Stolze, 2015). Tube well yields vary, with an average yield of 8 m³/h. Generally, very little technical information about tube wells in this area could be sourced, with inaccuracy and inconsistencies certainly posing a problem in the few available borehole logs. An evaluation of static water level data measured in different field campaigns combined with a numerical groundwater flow model has shown the relative groundwater flow direction to be from NE–SW towards the Mouhoun river (Stolze, 2015).

3. Methods

3.1. Hydrochemistry and stable isotopes (¹⁸O, ²H)

Within the study area, we located and sampled all existing community tube wells (equipped with hand pumps of the types India, Volanta or Vergnet, $n = 29$) and a selection of dug wells

($n = 4$). We followed standard sampling and laboratory analysis procedures as described in similar studies (Buschmann et al., 2007; Berg et al., 2008). On-site parameters (temperature, pH, electrical conductivity, O₂ concentration and redox potential) were measured in a flow-through cell connected to the hand pump spout. Water sampling was performed after on-site parameters had stabilised, generally after less than 10 min. All sampled tube wells are pumped nearly continuously during the day by local residents for drinking water, hence water was never stagnant in the pipes before sampling. Samples for major cations and trace element analysis (including As) were collected in acid-washed polypropylene bottles, filtered through 0.45 μm filters and acidified with concentrated HNO₃ suprapure to a pH < 2. An unfiltered, non-acidified aliquot was collected for the analysis of anions, dissolved organic carbon (DOC), total inorganic carbon (TIC) and stable water isotopes (²H, ¹⁸O). For As speciation, filtered samples were passed through an aluminosilicate cartridge which retains As(V) (Meng and Wang, 1998) and then acidified. Samples were stored below 4 °C whenever possible. Analysis was performed in the laboratories of Eawag, Switzerland, using ICP-MS (Agilent 7500 cx) for cations and trace elements, ion chromatography for anions (ICS-2001 Dionex) and a carbon analyser (TOC Shimadzu) for TIC and DOC. Measurement of ²H and ¹⁸O was performed using cavity ring-down laser spectroscopy (Picarro L1 102-I). After the initial sampling campaigns in February and April 2015, a selection of tube wells ($n = 19$) and dug wells ($n = 3$) were re-sampled in the months during and after the rainy season (August 2015 – February 2016) to investigate seasonal changes in hydrochemistry. Gaps in the dataset result from malfunctioning hand pumps or prolonged inaccessibility to the study site due to surface flooding during the rainy season. Seasonal changes in static water levels were only measured at dug wells and tube wells equipped with “India” type hand pumps which allowed easy access to the water table with a dipper. Hand pumps of the type “Volanta” and “Vergnet”

have to be dismantled and pump and tubing removed from the borehole before a dipper can be lowered.

3.2. Noble gas and tritium sampling and analysis

The noble gases He, Ne, Ar, Kr and Xe and the radioactive hydrogen isotope ^3H (tritium), act as tracers for environmental processes (Aeschbach-Hertig et al., 1999; Beyerle et al., 1999; Aeschbach-Hertig and Solomon, 2013). Their concentrations and isotope ratios in groundwater can give indications of groundwater dynamics, residence times and mixing ratios (Kipfer et al., 2002). Atmospheric noble gases dissolve in groundwater during recharge. The dissolution of entrapped air bubbles below the groundwater table may lead to a supersaturation of atmospheric noble gases with respect to equilibrium concentrations (excess air) (Kipfer et al., 2002; Aeschbach-Hertig and Solomon, 2013). Helium in groundwater can stem from several different reservoirs which have distinct $^3\text{He}/^4\text{He}$ isotope ratios. Atmospheric He ($^3\text{He}/^4\text{He} = 1.384 \times 10^{-6}$; Clarke et al., 1976) dissolves in groundwater during recharge, while radiogenic He

(He_{rad}) is a daughter product of the U-Th decay series and is constantly emanated from minerals in the Earth's crust. Radiogenic He may result from different sources: (1) produced in-situ in the aquifer (Andrews, 1985), (2) as external input from the Earth's crust ("crustal flux") (Torgersen and Clarke, 1985) and (3) as stored ^4He released from very old crustal rocks through weathering (Heaton, 1984) or diffusion (Solomon et al., 1996). Radiogenic He accumulates in groundwater, has a typical $^3\text{He}/^4\text{He}$ signature of 10^{-9} to 10^{-7} (Tolstikhin, 1984) and can be used to date groundwater with residence times $> 10^{2-3}$ years (Kipfer et al., 2002). Helium can also be emitted directly from the Earth's mantle in Rift zones or other volcanically and tectonically active regions and has He isotope ratios of around 10^{-5} (Mamyrin and Tolstikhin, 1984). Tritogenic ^3He ($^3\text{He}_{\text{tri}}$) is produced as a direct product of the radioactive decay of tritium (^3H , half-life 12.3 a), a process that can be used to date groundwater with short residence times (< 50 a) (Kipfer et al., 2002).

As noble gases are also present in the atmosphere, it is vital to avoid any air contact while sampling groundwater for noble gas analysis in order to avoid contamination. At the selected tube

Table 1
Summary of measured chemical parameters for tube wells and dug wells.

	Unit	Tube wells				Dug wells			
		Min	Max	Median	n	Min	Max	Median	n
Depth	m b.g.l.	36	89	57	20	6.7	13	7.4	4
pH	-	6.25	7.21	6.93	29	4.97	7.28	5.52	4
EC	$\mu\text{S}/\text{cm}$	195	624	399	29	52	485	217	4
O ₂	mg/L	0.13	6.30	1.02	29	0.8	3.93	3.86	4
Temp	$^{\circ}\text{C}$	30.3	32.9	31.3	29	29.4	30.9	30.4	4
Eh	mV	271	502	425	24	458	508	484	4
DOC	mg/L	<0.5	2.80	1.20	29	0.6	3.1	2.05	4
TIC	mgC/L	30	88	54	29	1.9	65.8	12.6	4
HCO ₃	mg/L	150	439	271	29	9	329	63	4
F	mg/L	<0.1	0.25	0.09	29	<0.1	0.17	<0.1	4
Cl	mg/L	<0.1	8.97	0.59	29	1.74	41.0	3.52	4
Br	mg/L	<0.1	0.05	0.05	29	<0.1	<0.1	<0.1	4
NO ₃	mg/L	<0.1	33.1	3.66	29	0.87	51.4	17.5	4
SO ₄	mg/L	<0.1	11.1	0.99	29	0.26	4.59	2.10	4
PO ₄	mg/L	<0.1	0.15	0.05	29	<0.1	0.40	<0.1	4
Li	$\mu\text{g}/\text{L}$	1.9	44.9	9.3	29	0.6	7.6	1.94	4
B	$\mu\text{g}/\text{L}$	<5	34.8	14.1	29	<5	22.1	<5	4
Na	mg/L	4.2	68.6	19.6	29	3.4	35.9	14.4	4
Mg	mg/L	9.8	41.5	19.9	29	1.55	19.4	4.45	4
Al	$\mu\text{g}/\text{L}$	0.8	16.3	4.3	29	12.3	22.1	41.6	4
Si	mg/L	7.6	28.3	19.7	29	6.67	28.1	7.15	4
K	mg/L	0.16	0.80	0.31	29	0.81	4.63	1.18	4
Ca	mg/L	15.4	56.8	35.6	29	2.4	40.6	8.4	4
V	$\mu\text{g}/\text{L}$	0.09	33.8	3.97	29	0.25	6.19	0.56	4
Cr	$\mu\text{g}/\text{L}$	<0.02	1.19	0.06	29	0.05	1.09	0.32	4
Mn	$\mu\text{g}/\text{L}$	0.09	147	3.18	29	13.6	46.5	20.0	4
Fe	$\mu\text{g}/\text{L}$	<0.3	2953	12.4	29	4.9	86.7	48.9	4
Co	$\mu\text{g}/\text{L}$	<0.02	1.32	0.03	29	0.18	2.71	2.23	4
Ni	$\mu\text{g}/\text{L}$	<0.02	1.98	0.19	29	1.14	3.53	3.05	4
Cu	$\mu\text{g}/\text{L}$	<0.1	3.25	0.40	29	0.5	2.8	1.33	4
Zn	$\mu\text{g}/\text{L}$	1.0	741	5.4	29	3.1	20.3	10.1	4
As(tot.)	$\mu\text{g}/\text{L}$	<0.02	333	2.83	29	<0.02	6.53	0.28	4
A(V)	%	94	100	99	18	60	89	75	4
Se	$\mu\text{g}/\text{L}$	<0.02	0.99	0.13	29	<0.02	0.08	0.045	4
Sr	$\mu\text{g}/\text{L}$	55	313	144	29	17	172	58	4
Mo	$\mu\text{g}/\text{L}$	<0.02	5.96	0.80	29	0.18	0.67	0.21	4
Cd	$\mu\text{g}/\text{L}$	<0.01	0.75	0.01	29	<0.01	0.02	<0.01	4
Sn	$\mu\text{g}/\text{L}$	<0.02	0.39	0.34	29	<0.02	0.38	0.36	4
Sb	$\mu\text{g}/\text{L}$	<0.02	0.94	0.09	29	0.11	0.16	0.12	4
Ba	$\mu\text{g}/\text{L}$	<0.1	265	0.70	29	8.6	147	28.2	4
La	$\mu\text{g}/\text{L}$	<0.01	0.05	0.01	29	<0.02	0.56	0.22	4
Ce	$\mu\text{g}/\text{L}$	<0.01	0.076	0.01	29	0.02	0.64	0.32	4
W	$\mu\text{g}/\text{L}$	<0.02	3.76	<0.02	29	<0.02	0.44	<0.02	4
Tl	$\mu\text{g}/\text{L}$	<0.02	<0.02	<0.02	29	<0.02	0.14	<0.02	4
Pb	$\mu\text{g}/\text{L}$	<0.02	0.21	0.04	29	<0.02	0.24	0.16	4
U	$\mu\text{g}/\text{L}$	<0.02	0.06	<0.02	29	<0.02	<0.02	<0.02	4
$\delta^{18}\text{O}$	‰ (VSMOW)	-5.56	-3.52	-4.37	17	-4.46	-3.95	-4.3	4
$\delta^2\text{H}$	‰ (VSMOW)	-36.2	-19.1	-26.0	17	-27.1	-23.9	-25.9	4

wells ($n = 12$), the hand pump and connected pipes had to be dismantled and removed from the borehole to allow for the insertion of a small submersible pump (type Comet-Combi) connected to a 12 V battery. The pump was typically installed 5–6 m below the water table at depths of 12–25 m below ground level. Groundwater was pumped until on-site parameters (temperature, pH, EC, O_2 , Eh) were stable and then filled into gas-tight copper tubes and tightly clamped (Beyerle et al., 2000). The analysis of noble gas concentrations (He, Ne, Ar, Kr, Xe), isotope ratios ($^3\text{He}/^4\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$, $^{36}\text{Ar}/^{40}\text{Ar}$) and ^3H was performed at the Noble Gas Laboratory of ETH Zurich by noble gas mass spectroscopy (Beyerle et al., 2000).

4. Results and discussion

4.1. Hydrochemistry

The sampled groundwater has varying hydrochemical signatures despite the close spatial proximity of the samples, with closest distances between tube wells being ~ 200 m. A summary of all measured parameters is displayed in Table 1. Tube well water has circumneutral pH (6.3–7.2), whereas dug wells generally show more acidic values (pH 5–6). Electrical conductivities range from 195 to 624 $\mu\text{S}/\text{cm}$ for tube wells, with only two dug wells having much lower mineralisation. Dissolved oxygen is generally present in a range of 0.1–2 mg/L for tube well water (few exceptions with higher values) and groundwater can be classified as oxic (Eh

380–500 mV). Three tube wells, on the other hand, have mildly reducing values of 270–290 mV and dissolved O_2 of 0.8–1 mg/L.

Arsenic concentrations above the WHO guideline value of 10 $\mu\text{g}/\text{L}$ were found in five tube wells, the highest concentration being 333 $\mu\text{g}/\text{L}$ (Fig. 2). The pH values of these high-As samples belong to the higher values measured (>7.0), with dissolved O_2 concentrations < 1 mg/L (one exception) (Fig. 2). No linear relationship between the depth of tube wells and As concentrations was seen. Similarly, no clear trends between As and any other measured parameter could be observed. An exception is antimony (Sb), where the highest concentrations were measured in the samples having elevated As (Fig. 3). Nevertheless, the measured Sb concentrations are still relatively low (< 1 $\mu\text{g}/\text{L}$). Relationships between dissolved Sb and As in groundwater (though with much higher Sb concentrations) have been described by Verplanck et al. (2008) and attributed to the co-occurrence of stibnite (Sb_2S_3) with arsenopyrite and pyrite in auriferous zones. Antimony ores are found in Burkina Faso, though are not specifically described in the area of Poura (Kote et al., 2003). However, Sb- and As-rich pyrites have been found in the Boromo greenstone belt at Gaoua, about 150 km south of Poura (Le Mignot et al., 2017). Antimony is probably a minor constituent of the mineralised zones in Poura and released together with As during sulphide mineral oxidation, though the aqueous geochemical behaviour of Sb is essentially different to that of As (Mitsunobu et al., 2006). The positive correlations between As and W and Mo concentrations observed in waters from auriferous zones in northern Burkina Faso by Smedley

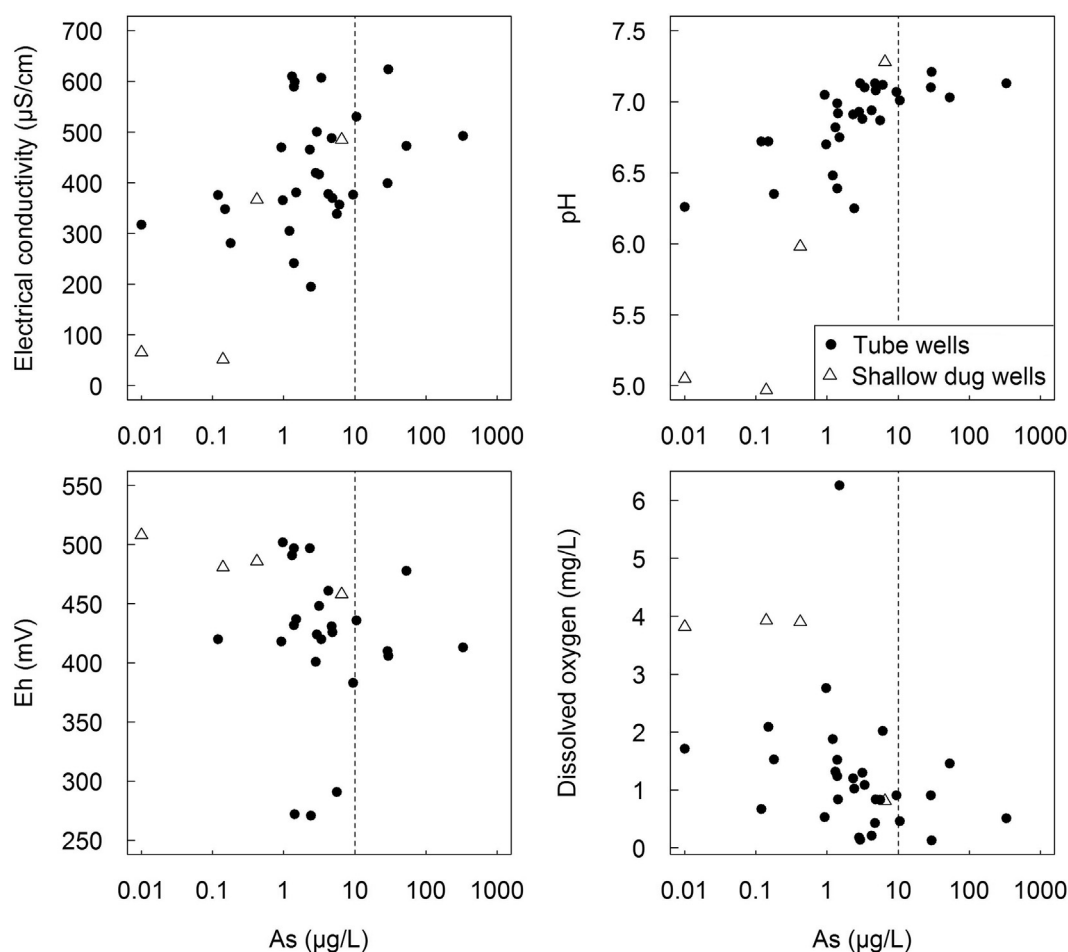


Figure 2. Scatter plots of groundwater arsenic concentrations versus pH, Eh, O_2 and electrical conductivity. Note the log scale on the x-axes. The dashed line represents the WHO drinking water guideline value for As of 10 $\mu\text{g}/\text{L}$ (WHO, 2011).

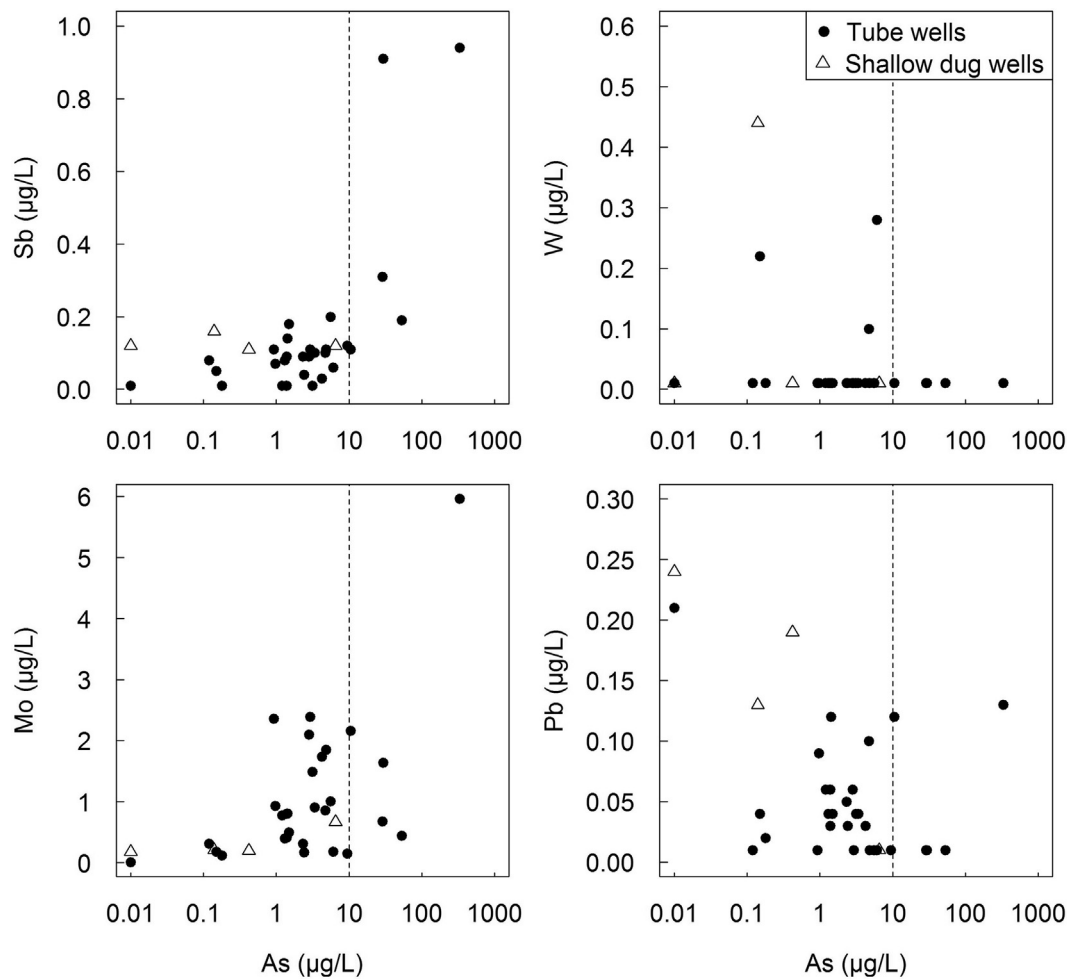


Figure 3. Groundwater As concentrations plotted against trace metals commonly found in Birimian auriferous zones (Sb, Mo, W, Pb) (e.g., Smedley et al., 2007; Le Mignot et al., 2017). The dashed line indicates the WHO drinking water guideline value for As of 10 µg/L.

et al. (2007) are not reproduced in Poura (Fig. 3), which may be due to regional differences in mineralisation and mineral assemblages.

Due to the oxic nature of the groundwater, As is predominantly found as As(V) (Table 1). In this state, and at circum-neutral pH, dissolved As chemistry is strongly controlled by sorption to Fe(III) hydroxides (Dixit and Hering, 2003). Dissolved Fe concentrations are generally also very low, with only three tube wells with mildly reducing signature having significant Fe concentrations (Fig. 4). These wells do not show elevated As though, indicating that reductive dissolution of As from Fe hydroxides is most likely not the source mechanism of high groundwater As. Even though the analysis of filtered and unfiltered samples revealed that some particulate Fe occurs (generally lower dissolved Fe concentrations in filtered than in unfiltered samples, Fig. 5), As does not seem to be bound to these iron hydroxide solids, as filtered and unfiltered As concentrations are nearly identical (Fig. 5).

The spatial variability of As concentrations is high and does not show any clear pattern. Highly contaminated wells (e.g. PO-1, 333 µg/L) can be found within a few hundred metres of uncontaminated wells (e.g. PO-2, 2.4 µg/L) (Fig. 6). This also reflects the very heterogeneous distribution of mineralised areas, which in Poura occur as gold and sulphides (mainly pyrite and arsenopyrite) associated to quartz veins. Such quartz veins may have widths of only a few metres to tens of metres and extend from a few hundred metres to several kilometres, with the surrounding metamorphic/

volcanic host rock being comparatively sulphide-free (Béziat et al., 2008). In addition, the As content of pyrites may vary greatly in the same location, demonstrated by Le Mignot et al. (2017), who measured pyrite As contents between 0.1 and 1178 ppm in drill cores samples ($n = 90$) at Gongondy, Gaoua district, 150 km south of Poura. As already postulated by Smedley et al. (2007), the direct proximity to mineralised zones (quartz veins with associated sulphides) must play a major role in influencing groundwater As concentrations. The observed dissolved As concentrations can only be explained by a very high As release in the direct vicinity of As-containing sulphides, as with increasing distance from the As source, dissolved As(V) should rapidly adsorb to Fe(III) hydroxides in the oxic, circum-neutral pH conditions. This can also partly explain the large variability in As concentrations over short distances.

The hydrochemical signatures of dug wells can also be very variable, reflecting the different layers of the aquifer, their geochemistry and state of weathering. The three shallowest dug wells (PO-18, PO-20 and PO-22, depths 6–7 m) source their groundwater from the upper saprolite layer, that is highly weathered. The water has very little geochemical evolution (low pH, low electrical conductivity, low concentrations of major elements, low As), is probably recently recharged and can be clearly distinguished from the tube well groundwater. By contrast, the deeper dug well (PO-14, 13 m) has a pH and element concentrations that are similar

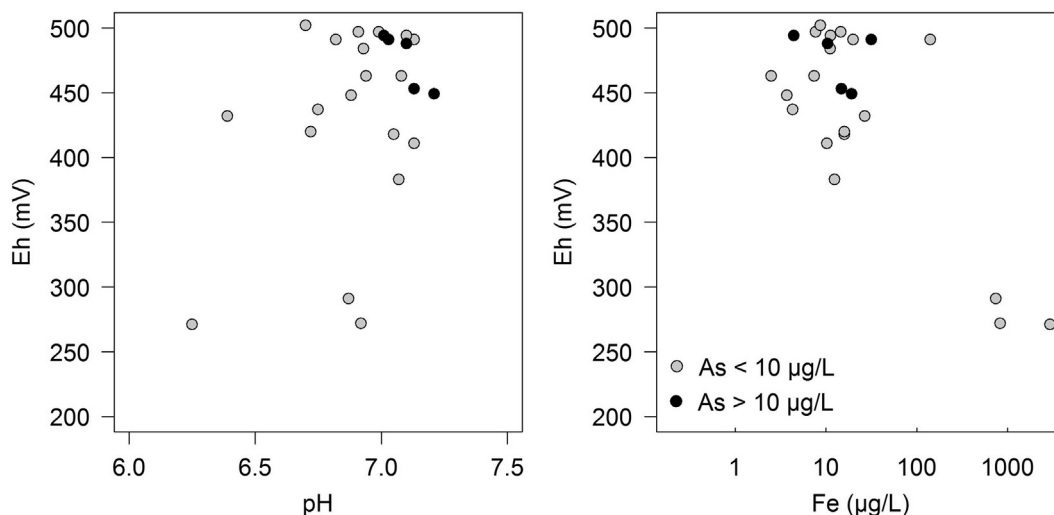


Figure 4. Redox potential of tube well water plotted against pH and dissolved Fe concentrations.

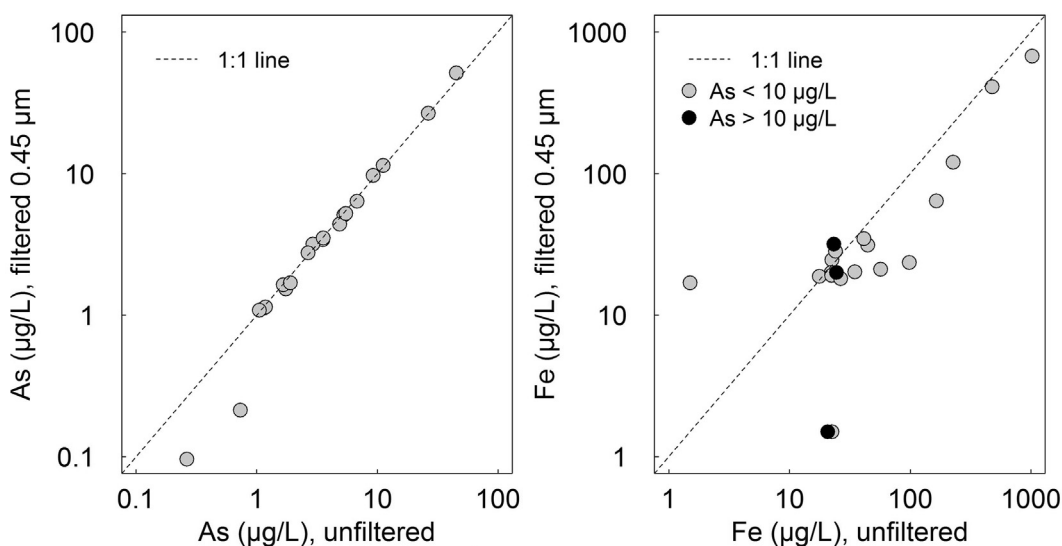


Figure 5. Arsenic and iron concentrations in filtered and unfiltered samples.

to those of groundwater tapped by tube wells (e.g. Figs. 2 and 3), as well as an elevated As concentration of 6.5 µg/L (rising to 12 µg/L during the rainy season, see section 4.4, Fig. 12). Clearly this well reaches geochemically more evolved groundwater from the lower saprolite. The geochemical signature of the laterite/ferricrete and saprolite layers can vary significantly at different sites, according to the chemistry of the bedrock but also due to the geomorphological evolution of the weathering profile (Bamba, 1996; Bamba et al., 2002). In addition to in-situ weathering of the parent rock, material eroded from hillslopes may be incorporated into the weathering profile, changing the geochemical signature of some layers. Bamba et al. (2002) found well-conserved sulphide minerals and still elevated As content in some ferricrete and saprolite (upper 12 m) in the vicinity of Poura, whereas other nearby profiles were depleted in most major and trace elements, and dominated by residual Fe and Al hydroxides. From the limited data available in this study and especially without analysing the geochemical composition of the aquifer material at the site of the sampled dug wells, it is not possible to draw conclusions on the main process governing the chemistry of dug well water. We hypothesise that the geochemistry

of the aquifer material plays a greater role than the (generally short) groundwater residence time, with elevated groundwater As concentrations occurring if sulphide minerals are still present in the saprolite. Where intense weathering has caused the dissolution of the sulphides and Fe and Al hydroxides predominate, the shallow, slightly acidic groundwater has very low mineralisation and As chemistry (if present) should be controlled by sorption to the abundant ferric material.

From a drinking water perspective, As is the only parameter of major health concern in the investigated groundwater samples. Elevated nitrate (NO_3^-) concentrations affect some dug wells and shallow tube wells, but only surpass the WHO drinking water guideline value of 50 mg/L (WHO, 2011) in the case of one dug well (Fig. 7). The five shallowest tube wells (<50 m) all have NO_3^- concentrations between 15 and 35 mg/L, whereas concentrations in tube wells > 45 m in depth stay below 5 mg/L (one exception) (Fig. 7). The sources of NO_3^- are most likely of anthropogenic origin, supported by the very low background concentrations in the deeper wells and a positive correlation between NO_3^- and Cl^- concentrations (Fig. 7). Wells are usually constructed in the direct

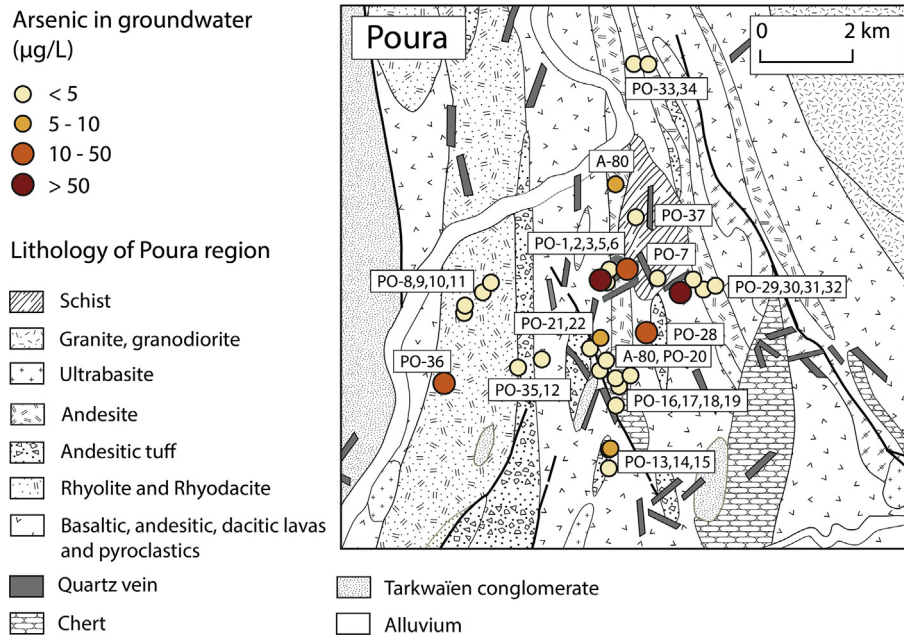


Figure 6. Map showing the variability in groundwater As concentrations, as well as the geological characteristics of the study area. Labels on the map refer to well IDs. Geological map source: Ouedraogo et al. (2003).

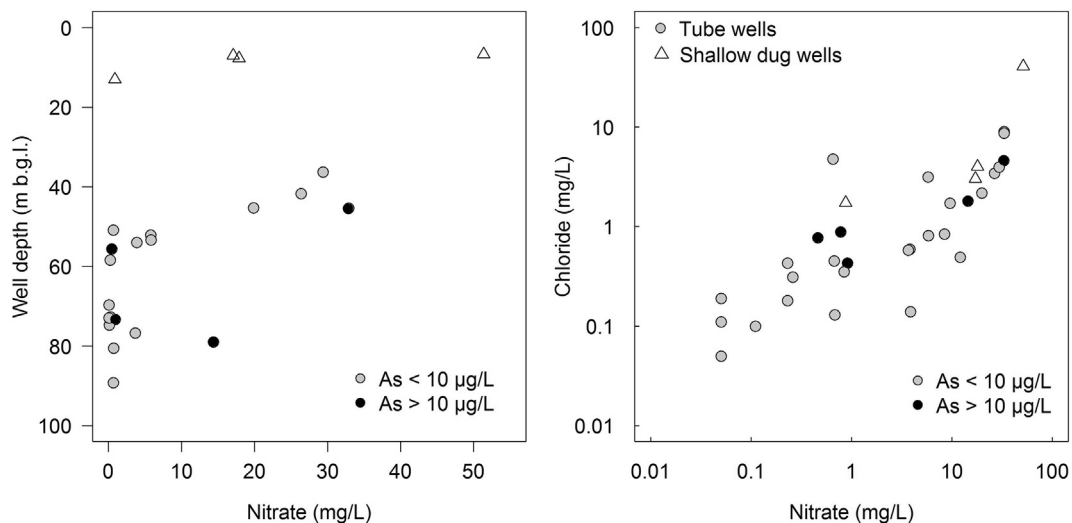


Figure 7. Groundwater nitrate (NO_3^-) concentrations plotted versus well depth and chloride (Cl^-) concentrations.

vicinity of human settlements without protection zones, and human and animal waste are most likely a direct source of NO_3^- to groundwater. Fertiliser application in the dominating subsistence agriculture is another possible NO_3^- source.

4.2. Stable isotopes (^{18}O , ^2H)

The stable water isotopes ^{18}O and ^2H are tracers for physical processes that water molecules may be subjected to in the hydrological cycle, such as evaporation, condensation, thawing and freezing. Stable isotope ratios in rainfall vary significantly globally, with these variations attributed to a number of usually temperature-related effects leading to isotope fractionation in large air masses (“continental effect”, “latitude effect” and “altitude effect”) (Rozanski et al., 1993). The isotope composition of tropical

rainfall, however, is less dependent on temperature, but rather related to the amount of rainfall (“amount effect”) (Dansgaard, 1964; Rozanski et al., 1993).

Time series of stable isotope measurements of rainfall are very scarce in the Sahel region of West Africa, with only two stations of the Global Network of Isotopes in Precipitation (GNIP), Bamako (Mali) and Niamey (Niger) having data spanning more than 10 years. Together with much shorter data series from the stations of Bobo-Dioulasso, Barogo, Houndé and Nasso in Burkina Faso, we determined the Local Meteoric Water Line (LMWL) for the study region (Fig. 8). The isotope ratios of precipitation have a very large range from -10‰ to 5‰ ($\delta^{18}\text{O}$) and -60‰ to 30‰ ($\delta^2\text{H}$). A clear “amount effect” can be observed for the collected precipitation values (Fig. 9). Sporadic rain events at the beginning and end of the dry season (May, June, September, October) are characterised by

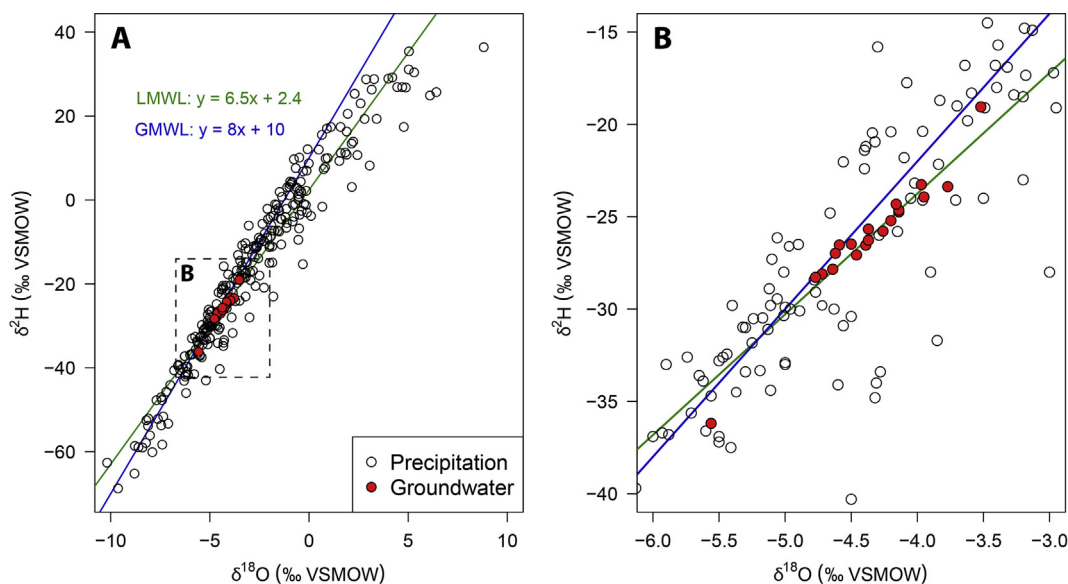


Figure 8. Stable water isotopes of the sampled groundwaters in Poura and of precipitation from the following GNIP stations: Burkina Faso: Bobo-Dioulasso (2010–2015), Houndé (2004–2005), Nasso (2004–2005), Barogo (1988–1989), Mali: Bamako (1962–1979, 1991–1998), Niger: Niamey (1992–1999, 2009–2015). LMWL: Local Meteoric Water Line, GMWL: Global Meteoric Water Line. Precipitation data source: Global Network of Isotopes in Precipitation (GNIP), IAEA/WMO. Fig. 8B represents a section of Fig. 8A as indicated by the dashed-line box.

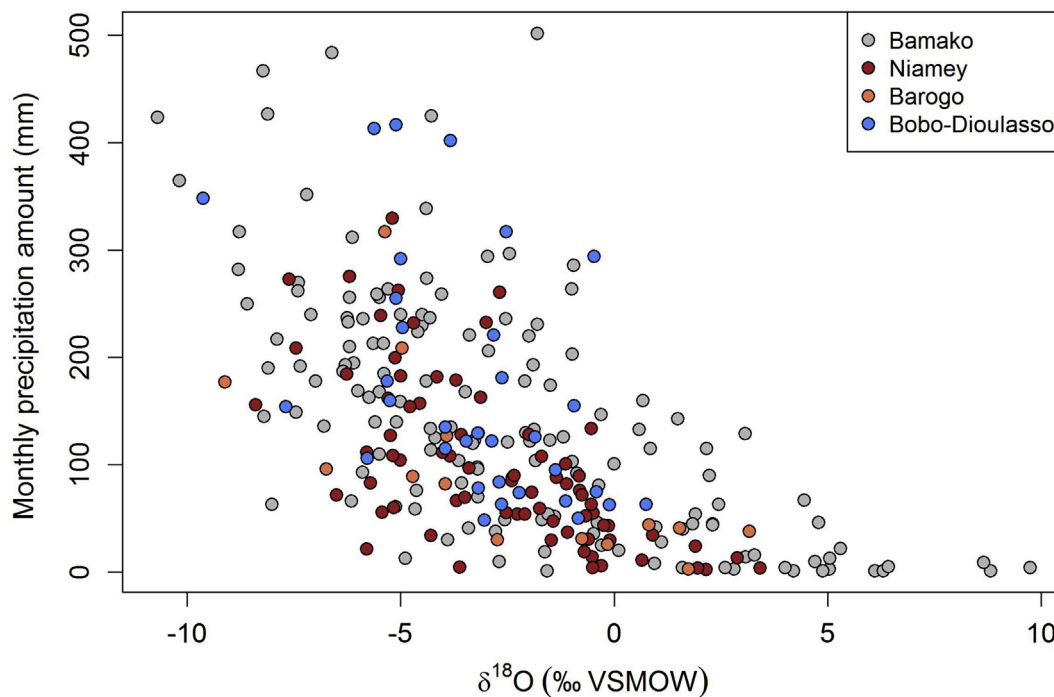


Figure 9. Monthly precipitation amounts from the GNIP stations Bamako (1962–1979, 1991–1998), Niamey (1992–1999, 2009–2014), Barogo (1988–1989) and Bobo-Dioulasso (2010–2015) plotted against the mean monthly stable oxygen isotope ratio, illustrating a clear “amount effect” in isotope fractionation.

enriched isotopic ratios, whereas the heavy and frequent rainfalls of July and August generally have more depleted values.

The groundwater samples from the Poura study site plot in the more depleted precipitation spectrum (Fig. 8), indicating that strong rain events during already humid conditions at the height of the rainy season most likely lead to groundwater recharge. This supports similar findings of authors investigating groundwater recharge mechanisms in tropical African aquifers (Taylor et al., 2013; Jasechko and Taylor, 2015). In addition, the

groundwater samples all plot on or near to the LMWL (Fig. 8), indicating that the water was not subjected to evaporation during groundwater recharge. This confirms observations made by other authors in the West African Sahel (Compaore et al., 1997; Beyerle et al., 2003; Huneau et al., 2011; Lutz et al., 2011; Lapworth et al., 2013) and supports the earlier conclusion that the Cl^- vs. NO_3^- relationship is probably pollution-rather than evaporation-influenced.

Table 2
Results of noble gas analysis. Measurement errors are typically between 1%–2% for total gas concentrations, about 0.1% for Ne and Ar isotope ratios and between 1%–3% for He isotope ratios.

Well ID	Well depth (m b.g.l.)	³ H TU	He [10 ⁻⁸] cc STP/g	Ne [10 ⁻⁷] cc STP/g	Ar [10 ⁻⁴] cc STP/g	Kr [10 ⁻⁸] cc STP/g	Xe [10 ⁻⁹] cc STP/g	³ He/ ⁴ He [10 ⁻⁶]	²⁰ Ne/ ²² Ne	⁴⁰ Ar/ ³⁶ Ar
PO-1	74	0.82 ± 0.07	6.50	2.54	3.18	6.24	7.75	1.61	0.1031	293.6
PO-37	45	n.d.	8.42	2.87	3.33	6.35	7.72	1.33	0.1031	292.6
PO-28	n.d.	n.d.	169	2.70	2.74	4.95	5.62	0.0796	0.1027	292.2
PO-30	46	1.81 ± 0.04	7.80	2.54	3.09	6.07	7.45	1.21	0.1029	293.7
PO-36	56	<0.5	205	2.37	3.11	6.23	7.58	0.0667	0.1030	293.6
PO-7	51	<0.5	283	2.83	3.46	6.88	8.32	0.0558	0.1031	294.3
PO-2	n.d.	1.53 ± 0.08	7.88	3.05	3.61	6.91	8.39	1.47	0.1033	293.6
PO-31	77	n.d.	37.1	12.3	8.78	13.6	14.1	1.25	0.1029	294.0
PO-17	73	<0.5	11.1	2.62	3.29	6.52	8.10	0.864	0.1030	294.5
PO-10	81	n.d.	46.5	4.40	4.32	7.98	9.46	0.358	0.1030	293.4

n.d.: not determined, STP: standard temperature and pressure, TU: tritium units.

4.3. Noble gases and tritium

Of the twelve noble gas samples obtained from tube wells during field work in February 2016, ten delivered reliable results. Two samples were apparently air-contaminated. The results reveal a very large range in He concentrations and ³He/⁴He ratios varying over three orders of magnitude, whereas the concentrations and isotope ratios of the atmospheric noble gases (Ne, Ar, Kr, Xe) are relatively similar for all samples (Table 2). For this reason, the focus of this section will lie on the presentation and discussion of the He results.

By plotting the ³He/⁴He ratio against the Ne/He ratio, potential noble gas end members can be identified (Fig. 10). The ten groundwater samples are spread on a nearly ideal two-component mixing line between He from atmospheric sources with high ³He/⁴He ratios and radiogenic He (⁴He_{rad}) characterised by very low ³He/⁴He ratios. The five samples close to the atmospheric He end member (PO-1, 2, 30, 31, 37) are shifted slightly to higher ³He/⁴He values than apparent from the mixing line (Fig. 10). This shift is likely induced by tritogenic ³He (³He_{tri}) production from the decay

of tritium (³H). Measureable ³H, though in low concentrations (0.8–1.5 TU), was determined in three of these samples (see Table 2). They most likely contain at least some water that was recharged after the 1950s. In all other samples, ³H was below detection (indicating pre-bomb recharge) or could not be determined due to high residual He concentrations in the samples after noble gas extraction. Such high residual gas concentrations usually occur when total He concentrations in the samples are high due to a dominance of radiogenic He, pointing to groundwater with long residence times and probably no or very little bomb-emitted ³H. One sample, PO-31, has clearly higher concentrations of the atmospheric noble gases (Ne, Ar, Kr and Xe) than all other samples (Table 2), which may be interpreted as the influence of excess air. This tube well has by far the largest water table fluctuation over the wet season of all monitored tube wells ($n = 8$) with a rise of at least 12 m, responding rapidly to the first rains (Fig. 12). Such a rapid water table rise can lead to the entrapment and partial dissolution of air bubbles from the unsaturated zone, resulting in the supersaturation of dissolved gases in groundwater (excess air) compared to atmospheric equilibrium (Heaton and Vogel, 1981; Ingram et al., 2007).

Three samples (PO-7, 28 and 36) stand out with very low ³He/⁴He ratios (Table 2, Fig. 10). Such dominance of ⁴He concentrations over ³He can only be explained by radiogenic ⁴He accumulation from U/Th decay. The influence of mantle-derived He can be ruled out, as its very high ³He/⁴He ratios of 10⁻⁵ (Mamyrin and Tolstikhin, 1984) are not observed in our samples, nor would mantle He be expected considering the geological conditions of the study area. If ⁴He_{rad} stems exclusively from in-situ, constant-rate production in the aquifer, the sampled groundwater must have been in contact with the minerals emanating ⁴He for very long timescales (> 10³ years) in order to accumulate such high ⁴He concentrations. By using the average U and Th concentrations of rock samples (andesite, dacite) in the study area (U: 0.4 ppm, Th: 1.1 ppm, database appendix to Ouedraogo et al. (2003)), we calculated a ⁴He production rate of 8×10^{-14} cm³STP/g_{rock}/a as demonstrated in e.g. Craig and Lupton (1976); Torgersen and Clarke (1985). By assuming a rock density of 2.5 g/cm³ and porosities ranging from 0.5% to 5% for an andesitic rock, we could further estimate groundwater age ranges of about 70–700 ka for sample PO-7, 40–400 ka (PO-28) and 50–500 ka (PO-36). These numbers are very rough indications only and may be overestimated if the other mentioned He sources (e.g. crustal flux or stored He, see section 3.3) also contribute to the total He concentrations. Local connections and discontinuities may exist to very deep fracture zones (as described, for example, in Courtois et al., 2010), that may act as conduits to He-rich fluids rising from deeper crustal layers. The Paleoproterozoic rocks with ages above 2 Ga that form the aquifers may have also accumulated a large ⁴He

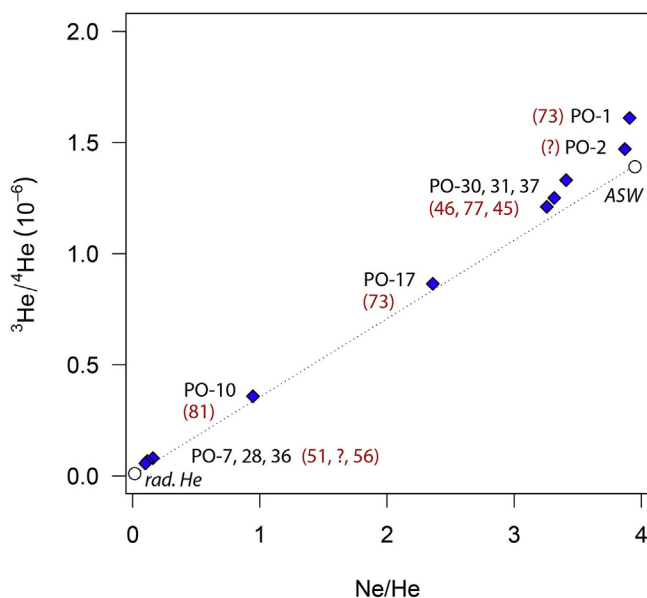


Figure 10. Helium isotope ratio and Ne to He ratio of the sampled groundwater. The dotted line represents the mixing line between the atmospheric (air-saturated water, ASW) and radiogenic He end members. Samples are labelled with the well ID (in black), the corresponding depth of each well (in metres b.g.l.) is given in brackets with red font.

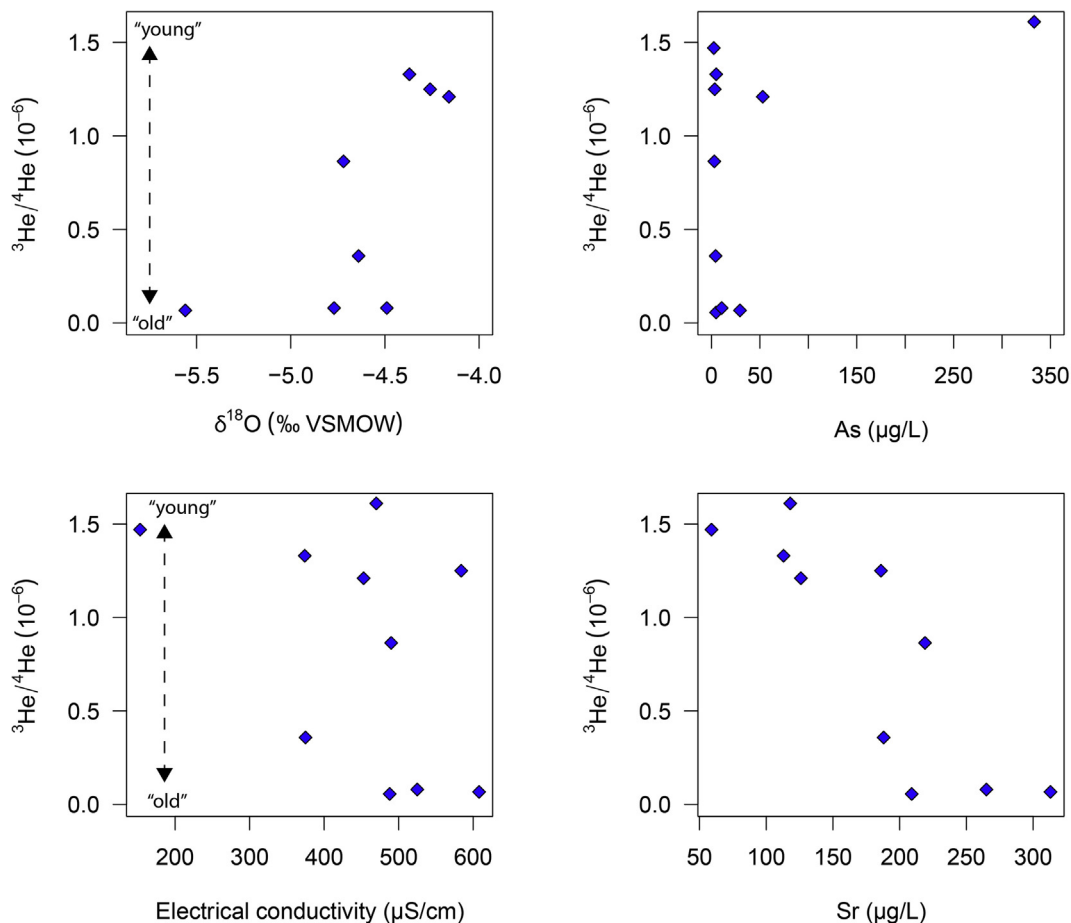


Figure 11. Helium isotope ratios ($^3\text{He}/^4\text{He}$) as an indicator of groundwater residence time plotted against other measured hydrochemical and isotopic parameters. The terms “young” and “old” refer to groundwater with short or long residence times as inferred from noble gas data.

pool (by U/Th decay) since their formation, some of which may be released over mineral surfaces during subsurface weathering. As explained in Section 2.2, the studied aquifers and their fracture porosity represent a deep weathering profile formed over many millions of years. Other studies have found though, that the He release due to weathering is insignificantly small compared to the in-situ production and crustal flux (Heaton, 1984; Torgersen and Clarke, 1985). Overall, we lack detailed information to accurately quantify the $^4\text{He}_{\text{rad}}$ accumulation and therefore cannot calculate a quantitative groundwater residence time. However, it can be assumed with some certainty that the samples with high ^4He concentrations contain portions of groundwater that had long residence times in the order of thousands of years and were cut off from the modern water cycle.

The tube wells with very low $^3\text{He}/^4\text{He}$ ratios do not follow a spatial trend in the study area and are found in close proximity to wells with a more modern signature. All sampled tube wells are similar in depth. In general, the most likely scenario to explain the high variations in ^4He concentrations is that some water-carrying fractures, even at depths of less than 50 m b.g.l. remain isolated from modern recharge and can carry very old, slow-moving groundwater. Groundwater exploited via the tube wells often represents a mixture of groundwater from different fissured zones (tube wells may be screened in two or three distinct sections (Stolze, 2015)), which is also visible in the atmospheric to radiogenic He mixing ratio presented in Fig. 10. The wells PO-10 and PO-17 most likely represent mixtures of groundwater with short and long residence times, while the fractions of modern water increase in samples plotting towards the

atmospheric-influenced He endmember. “Old” water dominates where samples plot towards the radiogenic He endmember.

It could be expected that groundwaters with residence times $>10^3$ years can also be distinguished from waters with much younger components by their hydrochemical and isotopic profiles. This is only the case to a certain extent. When comparing $^3\text{He}/^4\text{He}$ with $\delta^{18}\text{O}$ values, the “old” groundwaters have more depleted $\delta^{18}\text{O}$ values, though the differences to modern-influenced groundwater are only slight (Fig. 11). If groundwater had been recharged during a different, cooler climatic regime than at present, one would expect clearly more depleted $\delta^{18}\text{O}$ values than found in groundwater recharged by modern precipitation (e.g. Beyerle et al., 2003). The Sahel has certainly experienced periods of much cooler climate, though these have also alternated with climatic regimes similar to the present (Lézine and Casanova, 1989; Beyerle et al., 2003; Edmunds, 2009). Groundwater with residence times $>10^3$ years therefore does not necessarily have to display very different $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values to that fed by modern recharge. Supporting this statement, some groundwater samples with ^{14}C -ages >5 ka dated by Huneau et al. (2011) in sedimentary formations of south-west Burkina Faso and Mali using ^{14}C exhibited similar $\delta^{18}\text{O}$ values as modern groundwater. Similarly, no large differences were seen in $\delta^{18}\text{O}$ values of groundwaters in Mali and Senegal with ages ranging from modern to late Pleistocene (Edmunds, 2009). The sampled groundwaters in Poura most probably represent mixtures of old and some modern water, meaning that a more depleted $\delta^{18}\text{O}$ signature from a cooler climatic regime may be “diluted” by modern water portions with

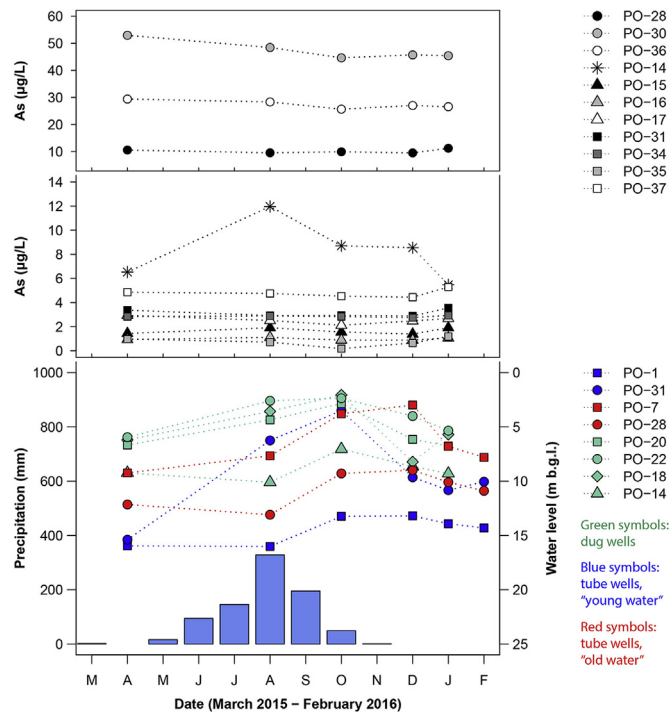


Figure 12. Top two graphs: Groundwater As concentrations measured in irregular intervals over the course of one year, from March 2015 to February 2016. Bottom graph: Static water level changes in a selection of tube wells and dug wells. The terms “young” and “old” water refer to groundwater with short or long residence times as inferred from noble gas data. The lowest water levels would be expected at the beginning of the rainy season, which cannot be seen in this data set as no samples exist from this period. The legend refers to the individual well IDs. Precipitation data is for the town of Boromo, about 25 km from Poura (Source: Direction Générale de la Météorologie du Burkina).

more enriched $\delta^{18}\text{O}$ values. No clear relationship can be observed between the degree of groundwater mineralisation as an indicator of prolonged water-rock interaction (given here as electrical conductivity (EC)) and groundwater residence time, though the three samples with low $^3\text{He}/^4\text{He}$ ratios have some of the highest EC values of all sampled tube wells (Fig. 11). Only strontium (Sr) shows some positive relationship with the $^3\text{He}/^4\text{He}$ ratios (Fig. 11), the old waters having higher Sr concentrations than water with modern influence. This is indicative of more mature groundwater with longer water-rock interaction.

Arsenic-affected tube wells capture groundwater with $^3\text{He}/^4\text{He}$ ratios spanning three orders of magnitude (Fig. 11). Elevated As concentrations are therefore found both in “old” groundwater, as indicated by very low $^3\text{He}/^4\text{He}$ ratios (tube wells PO-28, PO-36) as well as in tritium-containing, “modern” water (e.g. tube well PO-1, PO-30). Prolonged water-rock interaction, taking place over thousands of years in waters with long residence times, therefore does not seem to be a key factor in promoting elevated As concentrations. These results, in combination with hydrochemical data described in section 4.1, further support the hypothesis of previous studies (e.g. Smedley et al., 2007) that attribute elevated As concentrations (as As(V) in predominantly oxic waters) to result from sulphide mineral oxidation in auriferous zones. The proximity to such zones is most likely the main factor promoting the development of high As concentrations.

4.4. Seasonal changes

Very few data exist on the influence of the annual monsoon on groundwater hydrochemistry in the West African crystalline

bedrock aquifers. Specifically, temporal changes in As concentrations have not been investigated yet. Seasonal monitoring of groundwater levels revealed that tube wells in the study area respond differently to the monsoon. Gaps in the dataset do not allow a detailed interpretation, but general trends are visible. The water levels of some tube wells (e.g. PO-31) peak towards the end of the monsoon (October), whereas others only reach their highest level in December (PO-7), half a year after the onset of the rainy season (Fig. 12). The very late water level peak for the two tube wells abstracting water with long residence times (PO-7 and PO-28) is another indicator that these wells tap water from fractures that are at least partially isolated from modern, infiltrating water.

Results from hydrochemical sampling reveal that As levels in the study area do not vary greatly over the year (Fig. 12). A slight dip in concentrations can be observed in most wells during August–October, corresponding to the highest groundwater levels. Thus, there seems to be a slight dilution effect as uncontaminated water reaches the aquifer after the onset of the rains. As water levels recede again, concentrations stabilise. The only clear rise in As concentrations can be observed for the dug well PO-14, though this does not correspond to a rise in water level, which comes later (Fig. 12). Near-surface aquifers tapped by dug wells can be more vulnerable to fluctuations in water level, pH and redox conditions, possibly also affecting the mobility of trace elements.

5. Summary and conclusions

This study aimed to investigate arsenic-affected aquifers in fractured crystalline bedrock in West Africa by employing hydrochemical analyses in combination with isotope tracers. Results showed that a high variability in chemical and physical groundwater properties exist, influenced both by the geochemistry of the host rock (e.g. mineralised zones) but also by the highly heterogeneous fissured and fractured underground. Groundwater with varying elemental chemistry, redox conditions and residence times can co-occur over spatial scales of only a few hundred metres (Fig. 13). The application of noble gas tracers yielded new insights into the groundwater residence time distribution of these aquifers. In addition to modern, recently recharged groundwater with residence times of <50 years, we could show the existence of very old water portions with residence times $>10^3$ years already at depths of <50 m below ground level, representing non-renewable groundwater resources. This is valuable information, as previous studies generally attributed shallow groundwater in West Africa to dominantly have residence times of 30–60 years (Lapworth et al., 2013). We hypothesise that some water-bearing fractures remain disconnected from modern recharge and carry old, very slow-moving water. Discontinuities to the fresh, unweathered bedrock may also enable fluids from deeper layers to rise up (Fig. 13).

Elevated As concentrations (>10 $\mu\text{g/L}$) were found in oxic tube well groundwater with both short (<50 years) and long ($>10^3$ years) residence times and at different depths. The deepest of the four sampled dug wells also had a slightly elevated As concentration. Arsenic concentrations therefore do not seem to be influenced by groundwater residence time and increased water-rock interaction. In the absence of any clear correlations of As with other hydrochemical or isotopic parameters, we hypothesise that, in the observed oxidising conditions and at circum-neutral pH, solely the direct proximity to sulphidic mineralisations associated with quartz veins is relevant for generating the observed high As concentrations via sulphide oxidation. The annual monsoon season and associated changes in groundwater levels seem to have little effect on As concentrations in tube wells, with only a very slight dilution effect observed in some wells. For

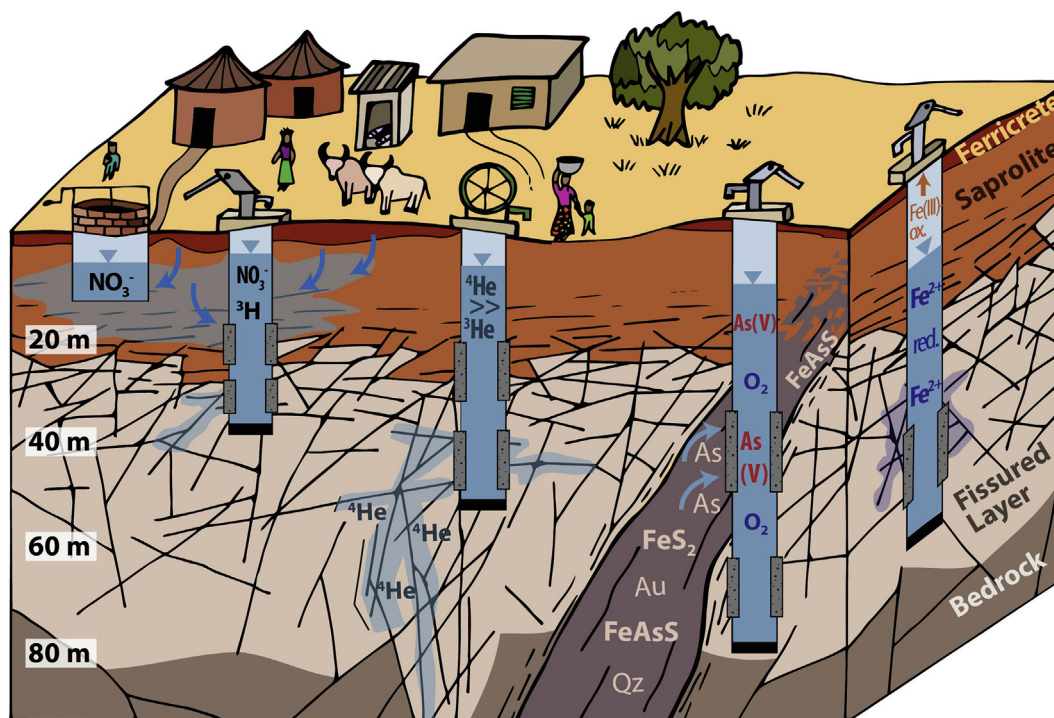


Figure 13. Overview diagram illustrating the highly variable physical and chemical groundwater properties observed in the study area. From left to right: (i) Groundwater in dug wells and shallow tube wells dominated by modern recharge and at times affected by pollution from settlements, livestock or agriculture. (ii) Tube wells tapping groundwater with long residence times ($>10^3$ years, high ^4He concentrations) from fractures isolated from the modern water cycle, possibly with connections to deeper crustal zones. (iii) Geogenic As contamination in wells directly dissecting mineralised zones, where As is released from sulphide minerals (FeAsS , FeS_2) by oxidation and found in oxic groundwater as dissolved As(V). (iv) Locally mildly reducing conditions ($E_h < 300$ mV) leading to high dissolved Fe concentrations and orange Fe(III)-precipitates when water is pumped and comes into contact with oxygen. The diagram is not drawn to scale.

drinking water provision, As remains of great concern. Affected wells are impossible to identify via factors such as well depth, redox potential, oxygen concentration or other hydrochemical parameters, therefore water analysis with advanced analytical techniques is always necessary. The alternative abstraction of groundwater via shallow dug wells cannot be recommended, as these may also contain As and are more vulnerable to nitrate and microbiological contamination. Large-scale groundwater quality surveys targeting As should be a focus for national authorities, especially in the Birimian mineralised zones where arsenic-affected groundwater is more likely to occur than in the large granitic terrains (Bretzler et al., 2017).

Extensive groundwater exploitation for irrigation and industrial purposes is still relatively rare in Burkina Faso. With a rapidly rising population and increasing industrial and agricultural development, groundwater use will certainly increase in the future (Barbier et al., 2006). Considerable capacity for groundwater storage exists in the aquifers of the Sahel and seasonal monsoonal rainfall is clearly responsible for widespread modern groundwater recharge (Leduc et al., 1997; Martin and Van De Giesen, 2005; MacDonald et al., 2012; Lapworth et al., 2013). The relatively low-yielding crystalline bedrock aquifers have previously been estimated as being resilient to increasing extraction rates and climate change (Martin and Van De Giesen, 2005; MacDonald et al., 2012). Nevertheless, in light of the results of this study and the fact that groundwater residence times are still very little investigated in these systems, this statement may be too general. Aquifers yielding water with residence times $>10^3$ years may certainly be vulnerable to unsustainable exploitation. Without the application of age-dating tracers such as noble gases, ^3H and ^{14}C , these waters are very difficult to identify, as their chemical signatures can be similar to those of water

containing higher fractions of modern recharge. The relatively small noble gas dataset of this preliminary study limits the depth of interpretation that is possible. Nevertheless, the results show that more in-depth studies involving age-dating tracers in the fractured bedrock aquifers of semi-arid West Africa are necessary to gain a more complete picture of groundwater residence times.

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